Chiral Phthalocyanines through Axial Coordination

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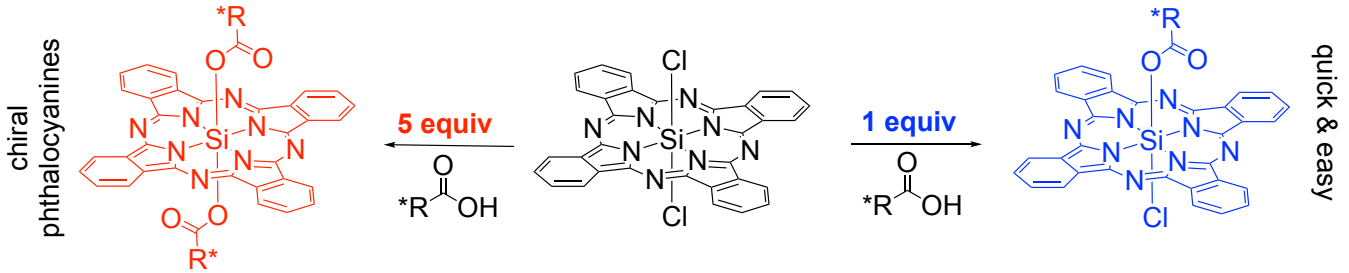
Supporting Information Placeholder



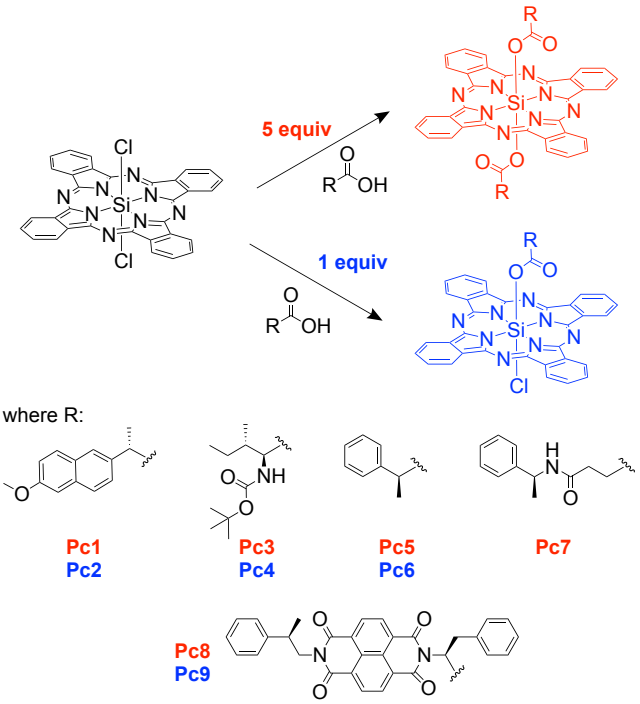
ABSTRACT: A novel approach to axially induce chirality on silicon phthalocyanines *via* a microwave-assisted route is reported. CD analysis provides spectroscopic evidence that chirality is transferred onto both Soret and Q-bands of the phthalocyanine core. A chiral naphthalenediimide ligand was found to induce the largest Cotton effect on the macrocycle absorptions.

Chirality plays a central role in science, spanning from life-regulating chemical processes and drugs to catalysis and supramolecular optical devices.[1,2] The insertion of chirality into planar achiral entities has been proposed as a powerful and accessible approach for tailoring optically active devices.[3–7] In light of this, phthalocyanines (Pcs), albeit intrinsically achiral, have emerged as ideal and versatile synthetic building blocks due to their unique electronic and spectral features.[8–10] Because of their thermal stability, chemical robustness and ability to self-assemble,[11] a plethora of synthetic routes toward generating optically active phthalocyanine derivatives have been put forward.[12,13] The current methods incorporate stereocenters into the peripheral positions of the Pc core,[14,15] or involve the introduction of substituents that distort the symmetry of the Pc macrocycle.[16] These synthetic routes are laborious, mostly low yielding, and employ harsh reaction conditions.[10,17–19]

An alternative approach to producing optically active Pcs consists of axial functionalization,[20–24] thus taking advantage of the free co-ordination sites of the metal cation. This has been less explored; to date only a few Sn and Ti[13] derivatives and an atropisomeric Zn-Pc complex with binaphthyl units[25] have been reported. While a few Si-Pcs[26–29] bearing chiral carboxylate units[30,31] on the Si co-ordination sites are reported in the literature, no study, or even observation, of their chiral nature is provided. The published syntheses of these Si-Pcs[30,31] require harsh conditions (*e.g.,* strong bases such as NaH, DBU) and prolonged reaction times that limit the number of chiral groups that can be appended using this method. In order for chiral Pcs to be considered for optically active devices, a more direct and high yielding synthesis is necessary.

We report herein a rationally designed approach for the efficient synthesis of chiral Si-Pcs (Scheme 1), as well as a comprehensive analysis of their absorption, fluorescence and circular dichroism properties. We have developed a one-pot, microwave-assisted protocol that uses the non-nucleophilic Hünig's base and short reaction times, and produces moderate to good yields of axially coordinated, chiral Si-Pcs. The synthetic route, depicted in Scheme 1, involves an exchange between chloride and carboxylate ligands on the Si center.

Scheme 1. General reaction protocol for synthesis of chiral phthalocyanines 1-9; color codes: red – di-substituted Pcs, blue – mono-substituted Pcs.



Mono- and dicarboxylate derivatives have been synthesized by varying the amount of carboxylic acid added to the commer-

cially available $PcSiCl_2$. Monocarboxylate-monochloro Si-Pcs are attractive, not only because of their chirality, but also because of the desymmetrization of the Pc core, which is then amenable for further functionalization. Table 1 summarizes the reaction conditions and yields obtained for each derivative.

Table 1 Reaction conditions and yields for Pcs1-9.

product name	equivalents of ligand	reaction conditions[a]	yield (%)
Pc1	5	155 °C, 14 h	68
Pc2	1	125 °C, 3 h	15
Pc3	5	155 °C, 14 h	83
Pc4	1	125 °C, 3 h	14
Pc5	5	155 °C, 14 h	63
Pc6	5	155 °C, 14 h	6
Pc7	5	155 °C, 14 h	33[b]
Pc8	5	155 °C, 14 h	42
Pc9	5	155 °C, 14 h	51

[a]All reactions were performed in dry toluene/DIPEA in the microwave as shown in Scheme 1. Detailed protocols for each derivative are in Supporting Information (SI). [b]This yield corresponds to a mixture of two conformationally different di-substituted derivatives.

The axial ligands have been selected based on the position of the stereocenter with respect to the ligation site (proximal or distal from the Pc core), as well as based on their level of saturation (aromatic and aliphatic scaffolds) in an effort to establish the best structural elements for inducing chirality on the Pc chromophore.

The typical ^{1}H NMR signature of an axially-substituted Pc displays a large up-field shift of the signals, corresponding to the protons closest to the Pc ring (*i.e.,* the protons in the α position relative to the carboxylate moiety). For example, in the case of **Pc8**, the dd (CH) at 2.86 ppm corresponding to the proton next to the carboxylate group (Figure 1, top) is the closest to the Pc unit, hence the most shielded with respect to its un-ligated chemical shift. This molecule (**Pc8**) exhibits unique spectral features, as half of the naphthalenediimide (NDI) moiety is in the proximity of the Pc core, thus explaining the up-field shift (δ 7.49 ppm) of these protons, compared to the rest of NDI's protons, which appear slightly deshielded (δ 8.39 ppm). The ^{1}H NMR spectra also provide a valuable tool in determining the ligand:Pc ratio; the 2:1 or 1:1 stoichiometry has been easily established based on the splitting pattern of the aromatic protons corresponding to the Pc ring, as well as the integration values of the ligand:Pc signals.

Single crystals, suitable for X-ray diffraction analysis, of **Pc8** have been obtained by slow evaporation of an acetonitrile solution. The molecule crystallizes in the tetragonal space group $P4_32_12$ with the carboxylate scaffolds arranged in *trans* geometry, and an NDI moiety parallel with the Pc core, as illustrated in Figure 1(a). Each NDI unit is packed in-between two Pcs, assembling into an extended aromatic π-π stacking fashion (Figure 1(b)). There are weak C-H···O=C interactions (2.98(2) Å, 137°) between the adjacent NDI units within the structure.

The structure of **Pc5** was also confirmed by X-ray diffraction crystallography of single crystals grown from $CHCl_3$. The molecule crystallizes in the orthorhombic space group $P2_12_12_1$ with the carboxylates moieties arranged in *trans* geometry with respect to each other (Figure 2). There are aromatic stacking interactions between the axial ligand's aromatic moiety and Pc macrocycle with an interplanar distance of 3.351 Å, and between the Pc cores of two neighboring molecules, with a distance of 3.379 Å. Two separate stacks are arranged in a herringbone-like fashion, as illustrated in Figure 2.

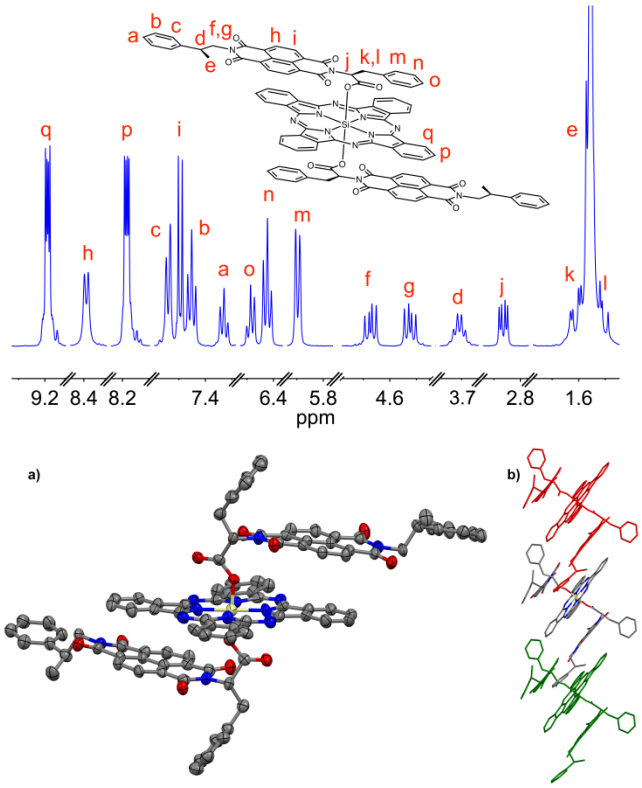


Figure 1. Top: the structure and labelled ^{1}H NMR spectrum of **Pc8** in $CDCl_3$ at room temperature. Bottom: a) ORTEP representation of **Pc8**. The thermal ellipsoids were drawn at 50% probability level (Hs were removed for clarity); b) fragment of the extended aromatic π-π stacking in the crystal packing of **Pc8**.

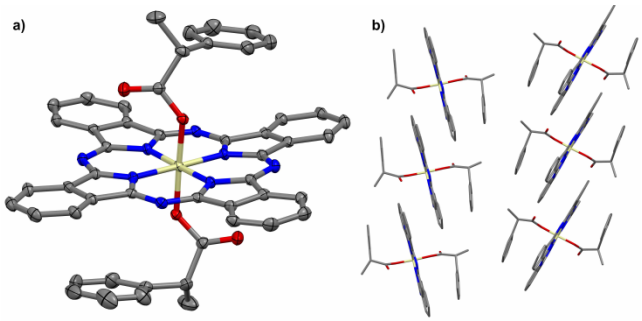


Figure 2. a) ORTEP representation of **Pc5**. The thermal ellipsoids were drawn at 50% probability level (Hs were removed for clarity); b) fragment of the herring-bone extended aromatic π-π stacking in the crystal packing of **Pc5**.

Circular dichroism (CD) is generally recognized as a valuable tool in assessing the chiral nature of a molecule, and together with UV-Vis spectroscopy, provides a unique insight into the opto-electronic and structural properties of chiral molecules.[32] The absorption spectra recorded in CH_2Cl_2 indicate that all of our derivatives exhibit the typical spectral features of phthalocyaninato-metal complexes (typical CD and UV-Vis spectra are illustrated in Figure 3 for **Pc9**), showing their non-aggregated nature (by sharpness of the band). The intense absorption band around 685 nm is the Pc's signature Q-band and corresponds to the lowest allowed $\pi \rightarrow \pi^*$ transition;[13] a weak vibrational shoulder at around 618 nm is also present.[13,17] The di-substituted derivatives are, as expected, slightly red-shifted, compared to the mono carboxylate ones, with **Pc8** having the most red-shifted absorbance (λ_{max} = 695 nm). The Soret band region displays weak broad bands across 332 – 382 nm that arise from $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions.[13,33] The NDI-functionalized Pc, **Pc8,** exhibits the most intense absorption in the Soret-band region, which accounts for the overlapping signals of Pc and the NDI core. All the UV-Vis spectra of the Pc derivatives studied are provided in the SI, and spectral features are summarized in Table 2. The spectroscopic fingerprints of our Pcs are consistent with previously reported data.[13,17,33,34]

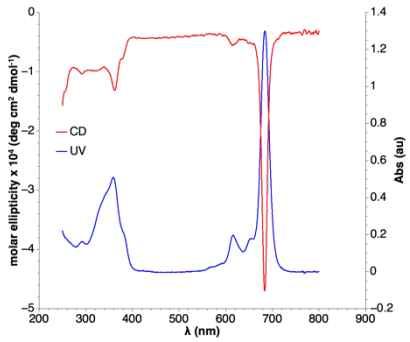


Figure 3. CD (red) and UV-Vis (blue) spectra of **Pc9** in CH_2Cl_2 (2.92 x 10^{-5} M).

Table 2. Spectral characteristics of Pcs1 – 9.

	Q-band characteristics			emission[b]	
product	λ_{max} (nm)	ε^a ($L \cdot mol^{-1} \cdot cm^{-1}$)	molar ellipticity × 10^4 ($deg \cdot cm^2 \cdot dmol^{-1}$)	λ_{max} (nm)	Φ
Pc1	688	234,000	-2.742	693	0.77
Pc2	682	60,000	-0.293	683	n/a[c]
Pc3	688	259,000	-0.749	693	0.79
Pc4	676	24,600	0.807	677	n/a[c]
Pc5	685	74,000	1.960	690	n/a[c]
Pc6	678	3,400	1.019	679	n/a[c]
Pc7	686	62,000	0.522	693	0.72
Pc8	695	115,000	4.436	673	0
Pc9	684	50,000	-4.907	671	0.28

[a]For error margins see Table S1 in the SI. [b]λ_{max} while exciting the Q-band. [c]Not available due to aggregation issues. The Φ of **Pc8** cannot be calculated because of the two NDI-based axial ligands which are fluorescence quenching.

Table 2 provides a direct assessment of the chiroptical properties of each mono / di-substituted Pcs pair. The CD spectra (provided in the SI) display a Cotton effect around 680 nm, which corresponds to the Q-band of the absorption spectra. This confirms that the chiral information is effectively transferred from the axial ligand to the Pc core. Without the axial chiral ligand, the Pc chromophore is in-plane polarized, and hence, intrinsically achiral, and would not have shown any CD signal at these wavelengths.[35] As expected, the Soret-type absorbance also shows a Cotton effect under the influence of the axial ligands.

The comparison of the molar ellipticities around 680 nm exhibited by the chiral Si-Pcs allowed us to identify the best ligand for chirality induction on the Pc chromophore. The NDI-functionalized Pcs (**Pcs8** and **9**) have the largest molar ellipticities (4.436 x 10^4 and -4.907 x 10^4 $deg \cdot cm^2 \cdot dmol^{-1}$ at 695 and 684 nm, respectively), which is potentially attributed to the intramolecular aromatic stacking interactions between the NDI and Pc cores restricting the molecular motions, as observed in the crystal structure of **Pc8** (Figure 1, bottom). The other aryl-based di-substituted derivatives (**Pcs 1** and **5**) have also exhibited an excellent ability to induce chirality due to their propensity to form aromatic stacking with the Pc ring; the crystal structure of **Pc1** previously reported by Sosa-Sánchez *et al.* confirms this hypothesis.[30] The position of a stereocenter relative to the co-ordination site is highly influential, as can be seen in the lower molar ellipticity exhibited by **Pc7**, where the stereocenter is far away from the Pc ring.

The only aliphatic ligand (isoleucine) of the di-substituted molecules series has one of the weakest CD signals, albeit its stereocenter is also located in the β position with respect to the Pc. This consolidates our assumption that the presence of the aromatic moieties is beneficial for generating chirality on the Pc's Q-band.

The fully desymmetrized mono-substituted analogues (**Pcs2**, **4**, **6**, **9**) are generally less soluble and more prone to aggregation than the di-substituted derivatives. The Q-band extinction coefficients of all the mono derivatives are an order of magnitude lower than their di-substituted counterparts. A similar trend is observed for the molar ellipticities measured on the Q-band absorbance (Table 2 and SI).

The emission and excitation spectra of Pcs in CH_2Cl_2 display similar spectral characteristics, except for **Pcs 8** and **9** which can be considered anomalies due to the fluorescence quenching nature of the NDI core. All fluorescence spectra are provided in the SI, and Table 2 summarizes the emission maxima upon excitation of the Q-band, along with the quantum yields calculated using Rhodamine 800 as the standard.

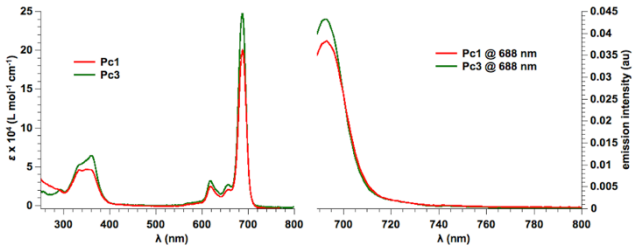


Figure 4. a) Overlaid UV-Vis spectra (CH_2Cl_2, 20 °C) of **Pc1** and **Pc3**; b) normalized emission of **Pc1** and **Pc3** in CH_2Cl_2 excited at the wavelengths described in the legend.

In summary, we report a novel approach to induce chirality *via* the axial positions onto intrinsically achiral Pcs. We have synthesized a series of mono- and di-substituted chiral Si-Pc derivatives, using a one-pot microwave-assisted protocol. The synthesis employs milder conditions and results in superior yields compared to the traditional methods. The optical and chiroptical properties of these molecules make them interesting candidates for chiral opto-electronic applications. The monocarboxylate-monochloro Si-Pc derivatives are particularly interesting because of their total asymmetry, which can be exploited for further functionalization.

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.or- glett.XXXXX. Experimental procedures and spectroscopic data for all the compounds discussed in the manuscript.

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The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

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